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DIFFUSION PHASE COMPETITION – FUNDAMENTALS
(Review)

The problem of initial stages of reactive diffusion is treated. The phase growth/suppression criteria due to diffusion interaction are analyzed. Some methods of incubation time calculation are proposed. The role of metastable phases at the initial stage is analyzed.

Розглядається проблема початкових стадій реакційної дифузії. Аналізуються критерії росту та пригнічення фаз внаслідок дифузійної взаємодії. Пропонуються способи обчислення інкубаційних періодів. Аналізується роль метастабільних фаз на початковій стадії.

Рассматривается проблема начальных стадий реакционной диффузии. Анализируются критерии роста и угнетения фаз вследствие диффузионного взаимодействия. Предлагаются способы расчета инкубационных периодов. Анализируется роль метастабильных фаз на начальной стадии.

Keywords: *diffusion, reaction, nucleation, phase competition, incubation time, growth/suppression criterion.*

Introduction

Reactive diffusion is the diffusion-controlled growth of intermediate phase layers between two reacting materials proceeding due to interdiffusion through the growing reaction products. Studies of reactive diffusion started in 1920s when the parabolic law of layer growth was discovered by Tammann. Evans found the possibility of mixed linear-parabolic regime. Wagner, Frenkel and Sergeev suggested the derivations of parabolic law. After World War II the late stages of reactive diffusion were investigated by Pines, Kidson, Geguzin, van Bastin, van Loo, Gurov, Ugaste.

Starting from 1980s the main interest of diffusion community steadily shifts from the problems of interdiffusion in solid solutions to the diffusive phase growth during interdiffusion (reactive diffusion) in the systems with limited solubility and the whole range of intermediate phases. In this review we treat the history of some ideas which appeared in the early 1980s and became a basis of new approach to the synergy of diffusion and reactions [1-32]. This review is not by far the complete story about reactive diffusion. It reflects authors' personal view and is based on the traditions of the diffusion schools of the former Soviet Union. After 1990, when our group and simultaneously the group of Pierre Desre and Fiqiri Hodaj started to modify the nucleation theory for the case of initial stages of reactive diffusion at nanoscale, much more intereting results have been obtained [7,33-43]. In this review we will almost omit these developments (which include rather intensive mathematical analysis) and concentrate over rather naïve but physically clear ideas about interrelation between diffusion, reactions and nucleation.

1. Standard model and anomaly problem. Reactive diffusion (formation and growth of intermediate phase layers in the diffusion zone as a result of interdiffusion of components through these layers) is a typical example of solid state reaction. It is notable for its reaction product - a crystal (generally, a polycrystal) of an intermediate phase rather than individual molecules (as in gas phase reactions) appears. The crystal remains at the site of the reaction and becomes a barrier to its further passing. For the reaction to proceed (when it is thermodynamically favorable) atoms have to diffuse through new-formed phase layers and react at one of the new-formed interfaces. The thicker the layers are the more time it takes to diffuse. And, therefore, the reaction goes more slowly. Thus, even at sufficient amount of reagents the phase growth rate decreases with time. It has become known since 1920s that in most cases the phase layer growth obeys parabolic law. We briefly review the standard model for the phase growth kinetics [1, 2].

First, consider the case of phase 1 growing within narrow concentration range $\Delta c = c_R - c_1 \ll 1$ at the process of annealing of a sample couple containing almost mutually insoluble materials A, B (let A component be on the left, and B component on the right). Thus, we'll neglect interdiffusion fluxes in the initial components of diffusion couple. Thereby, we consider all A atoms, which "managed to diffuse" to the 1/B boundary, to react with B atoms and not to go further, growing the phase "on the right". In the same way, B atoms, which "managed to diffuse" to the A/1 boundary, react with A and grow the phase "on the left". Let's neglect the molar volume changes at intermetallic formation, as, thus, right away disregard those effects that are connected with stresses, arising at phase boundaries. Besides, we'll consider the condition of diffusion flux steadiness to be fulfilled over the phase thickness. In other words, the distribution of components in the phase layer is quasi-stationary. One can prove this assumption [46], but it would be easier to get it in unsophisticated way. Indeed, since homogeneity interval of the intermediate phase is narrow (too large deviations from stoichiometric composition are energetically unfavorable), concentration "has no way out" and it keeps itself almost constant (close to stoichiometry) over the whole phase layer. That's why the time derivative of concentration is small, and so the flux divergence is close to zero. In one-dimensional case (diffusion couple) the divergence is simply equal to derivative over diffusion coordinate. The derivative's being equal to zero denotes that the flux density almost doesn't change over the whole phase layer. This means that the product of interdiffusion coefficient and concentration gradient is nearly equal everywhere inside the phase. Still, this doesn't imply that concentration gradient is equal everywhere, as interdiffusion coefficient may considerably change even at little deviations from stoichiometry (especially in phases of B2 - type, for example, NiAl). Hence, it's generally incorrect to simply say (as it's typically said and written) that concentration profile inside the phase is linear. Let's make elementary transformations. If a certain value is constant, it can be taken both inside and outside the integral sign. We'll take it inside the integral sign:

$$\Omega J = -\widetilde{D}\frac{\partial c}{\partial x} \approx \mathrm{const} \equiv \widetilde{D}\frac{\partial c}{\partial x}\frac{\int_{x_L}^{x_R} dx}{\int_{x_L}^{x_R} dx} = -\frac{\int_{x_L}^{x_R}\widetilde{D}\frac{\partial c}{\partial x}dx}{\int_{x_L}^{x_R} dx} = -\frac{\int_{c_L}^{c_R}\widetilde{D}dc}{x_R - x_L} \tag{1.1}$$

The value $\int_{c_L}^{c_R} \widetilde{D}dc$ is called Wagner's integral coefficient and is often written in the following way:

$$\int_{c_L}^{c_R} \widetilde{D}dc = D_1 \Delta c_1, \tag{1.2}$$

where $D_1 \equiv \dfrac{\int_{c_L}^{c_R} \widetilde{D}dc}{\Delta c_1}$ – effective diffusion coefficient averaged over the phase.

We emphasize once more that, as a rule, the kinetics of solid state reactions isn't determined by the diffusion coefficient and the homogeneity zone width separately but always by their product (i.e. the integral coefficient). And this is good comparison with experiment, for the homogeneity zone width in many phases is so narrow that it seems almost impossible to measure it experimentally. Wagner's integral coefficient can be transformed using Darken's relation, expressing interdiffusion coefficient in a binary system with tracer diffusion coefficients and the second derivative of Gibbs potential (per one atom) g with respect to concentration:

$$\widetilde{D} = (cD_A^* + (1-c)D_B^*)\frac{c(1-c)}{kT}\frac{\partial^2 g}{\partial c^2} \tag{1.3}$$

Having substituted this expression into Wagner's integral coefficient, considering the narrow phase homogeneity range, one gets:

$$\int_{c_L}^{c_R} \widetilde{D}(c)dc = \overline{D}_1^* \frac{c_1(1-c_1)}{kT}\left(\frac{\partial g}{\partial c}\Big|_{1,B} - \frac{\partial g}{\partial c}\Big|_{A,1}\right) \cong$$
$$\cong \overline{D}_1^* \frac{c_1(1-c_1)}{kT}\left(\frac{g_B - g_1}{1-c_1} - \frac{g_1 - g_A}{c_i - 0}\right) = \overline{D}_1^* \frac{\Delta g_1(A+B \to 1)}{kT} \tag{1.4}$$

Here $\overline{D}_1^*$ is diffusion coefficient of marked atoms averaged over the phase $\overline{D}_1^* \equiv c_1\overline{D}_A^* + (1-c_1)\overline{D}_B^*$, $\Delta g_1(A,B \to 1)$ is thermodynamic driving force (per one atom) of phase 1 formation (from A and B).

Thus, the growth rate of the single intermediate phase is determined by the mobility of atoms in it (tracer diffusivities) and by Gibbs energy of phase formation. As we can see, the "elusive" homogeneity interval itself is of little importance for us.

In such a way, the product of the density of B flux through phase layer and atomic volume (that is, "the flux density of the volume transferred by B atoms") equals to

$$\Omega J_B = -\frac{\int_{c_L}^{c_R} \widetilde{D}dc}{\Delta x_1} = -\frac{D_1 \Delta c_1}{\Delta x_1} \tag{1.5}$$

As is well known, the rate of interface movement is equal to the ratio of the fluxes step at this boundary to the concentration step. We regard the fluxes in marginal phases of the diffusion couple to be zero (negligible solubility). So the fluxes balance conditions at interfaces bring to the following two differential equations:
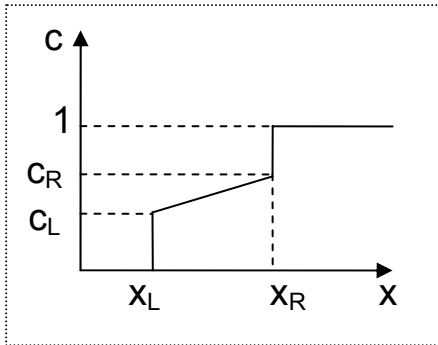
Fig. 1.1. Concentration profile at one phase growing between insoluble components.

$$(1 - c_R)\frac{dx_R}{dt} = \frac{D_1 \Delta c_1}{\Delta x_1}$$

$$c_L \frac{dx_L}{dt} = -\frac{D_1 \Delta c_1}{\Delta x_1} \qquad (1.6)$$

From these equations one can easily derive the differential equation for the phase thickness $\Delta x(t)$:

$$\frac{d\Delta x}{dt} = \frac{a}{\Delta x(t)}, \qquad (1.7)$$

where

$$a = \frac{1 - \Delta c_1}{(1 - c_R)c_L} D_1 \Delta c_1 \approx \frac{D_1 \Delta c_1}{c_1(1 - c_1)}. \qquad (1.8)$$

And this gives the well-known parabolic law of phase growth

$$(\Delta x)^2 = (\Delta x_0)^2 + \frac{2 D_1 \Delta c_1}{c_1(1 - c_1)} t. \qquad (1.9)$$

If the thickness of the layer considerably exceeds the initial thickness (the latter is taken right after the nucleation and lateral growth with formation of primary continuous layer), then

$$\Delta x \approx \sqrt{\frac{2 D_1 \Delta c_1}{c_1(1 - c_1)} t} \qquad (1.10)$$

Now, let's treat the case of two phases, 1 and 2, growing between two mutually insoluble metals. Here we again make the assumption of constant fluxes over the thickness of each phase (steady-state approximation):

$$\Omega J_B^{(1)} = -\frac{D_1 \Delta c_1}{\Delta x_1}; \Omega J_B^{(2)} = -\frac{D_2 \Delta c_2}{\Delta x_2} \qquad (1.11)$$

Equations of particle number balance at interfaces have the following form:

$$(1 - c_R^{(2)})\frac{dx_{2R}}{dt} = \frac{D_2 \Delta c_2}{\Delta x_2},$$

$$(c_L^{(2)} - c_R^{(1)})\frac{dx_{2L}}{dt} = -\frac{D_2 \Delta c_2}{\Delta x_2} + \frac{D_1 \Delta c_1}{\Delta x_1}, \qquad (1.12)$$

$$(c_L^{(1)} - 0)\frac{dx_{1L}}{dt} = -\frac{D_1 \Delta c_1}{\Delta x_1}.$$

It's quite easy to obtain the system of differential equations for phase thicknesses from Eqs. (1.12):

Fig.1.2. Concentration profile at two phases growing between insoluble components.

$$\frac{d\Delta x_1}{dt} = a_{11}\frac{D_1 \Delta c_1}{\Delta x_1} + a_{12}\frac{D_2 \Delta c_2}{\Delta x_2}$$

$$\frac{d\Delta x_2}{dt} = a_{21}\frac{D_1 \Delta c_1}{\Delta x_1} + a_{22}\frac{D_2 \Delta c_2}{\Delta x_2} \qquad (1.13)$$
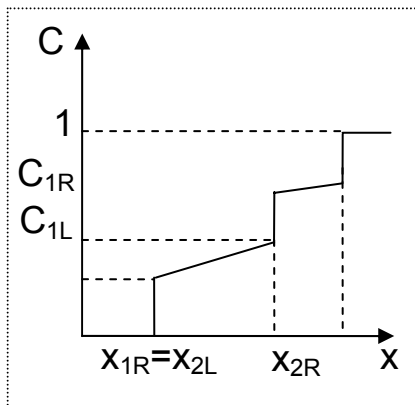
Here

$$a_{ik} = \begin{pmatrix} \dfrac{c^{(2)}}{c^{(1)}} & -1 \\ -1 & \dfrac{1-c^{(1)}}{1-c^{(2)}} \end{pmatrix} \dfrac{1}{c^{(2)} - c^{(1)}} \qquad (1.14)$$

It's easy to make sure that the equation system (1.13) has parabolic solutions as well, $\Delta x_1 = k_1 t^{1/2}, \Delta x_2 = k_2 t^{1/2}$, however, expressions for parabolic growth constants k_1, k_2 are not so "elegant" as in the Eq. (1.10) for the growth of one phase. Basic equations for any number of phase layers, growing simultaneously, are obtained in the same way. However, the mentioned simultaneity presents some problems that have become crucial since 1970-1980s with technological development of integrated chips manufacture and maintenance.

Standard model is quite sufficient to describe the late stages of reactive diffusion in standard "infinite" diffusion couple (with size much larger than the width of diffusion zone). Yet, since 1970s, the main field of reactive diffusion applications shifted to microelectronics, which uses reactions in thin films. Researchers immediately found that in this case standard model does not work, demonstrating various "anomalies" (sequential phase growth, deviations from parabolic law etc.) Such problems lead to reconsideration of standard model. It was made almost simultaneously by Gurov and Gusak [3], Gösele and Tu [4], V. Dybkov [5].

According to [5, 6], diffusion theory proves to have such a principle drawback, so that it doesn't explain (a) disagreements between the observed phase composition in the diffusion zone and that of the phase diagram; (b) breaking of a parabolic law for phase layer growth. Obviously, the author of [5, 6] might not have paid attention to the works [3, 4], which provide appropriate explanation for the facts mentioned above. And, to our mind, a number of the author's [5, 6] statements and predictions, appear to be disputable or simply incorrect.

In [5, 6] the diffusion theory is blamed for poor regard to "chemical phenomena" in the "chemical process". Here the reactions at layers boundaries are meant. If so, the problem must be specified. Reactions in the diffusion zone at formation and growth of phase layers, can be divided into two types:

reactions of the first type – formation of new phase nuclei in the contact zone as a result of heterophase fluctuations at chemical potential and concentration gradients;

reactions of the second type – those being "reactions" at the moving boundary of already existing phases, comprising of three successive steps: detachment of atoms from a lattice of a phase (I), transition through the interface (II), and attachment to the lattice of another phase (III).

Those are the reactions of the second type that are often meant, explicitly or implicitly, when "finite reaction rate" or "boundary kinetics" [4, 5, 6, 8-11] are taken into account. It makes sense to treat their influence on the process kinetics only in case of the "reaction" stage being limiting, i.e. characteristic time of detachment, transition and attachment of atoms is more or at least commensurate to that of diffusion delivery of both sorts of atoms at the interface.

Interface transition time is $\tau_1 \sim \dfrac{h^2}{D_B}$, where $h \sim 5 \cdot 10^{-10}$ m. Attachment time τ_2, at the worst, is reduced to time required for searching the "appropriate place" (grain-

boundary dislocation, etc.): $\dfrac{d^2}{D_B}$, d being equal to several atomic distances.

Detachment time, obviously, is close to τ_2 by the order of magnitude. Characteristic time of transfer through the layer

$$\tau_{dif} \sim \frac{\Delta x}{v} \sim \frac{\Delta x}{\dfrac{D\Delta c}{\Delta x}} \sim \frac{\Delta x^2}{D\Delta c}$$

(D - effective interdiffusion coefficient in the layer). Boundary kinetics appears to be limiting in case of $\tau_1 + 2\tau_2 > \tau_{dif}$, i.e. at

$$\Delta x < (h^2 + 4d^2)^{1/2} (\frac{D\Delta c}{D_B})^{1/2}.$$

According to the relation (1.4), $D\Delta c \approx D^* \dfrac{\Delta g}{kT}$, where D^* is a combination of self-diffusion coefficients of the components in the phase. If there is no oxide film or other barrier layer at the interface, then, as it is known, $D^*/D_B \ll 1$. So, (taking into account that h and d make a few atomic distances) the thickness of the phase layer Δx^*, at which the change from boundary kinetics to diffusion regime takes place, doesn't exceed the interatomic distance.

Apparently, the situation must radically change when treating the reaction between a solid body and a gas. In this case the boundary kinetics regime (and linear phase growth) can be reached by reducing the reagent's partial pressure in the gas medium which leads to atoms come at the surface.

In the contact zone of solid bodies the boundary kinetics, connected with reactions of the second type, can be expected only in the presence of oxide films or other barrier layers at the interface. We developed alternative idea for the long stage of linear growth [44,45]. It presents a certain interest, for it regards the limited power of interfaces as sinks/sources of vacancies, and corresponding contribution of non-equilibrium vacancies.

In other cases the regime of phase layer growth is a diffusion controlled one from the very beginning, if the beginning implies the already formed layer of new phase nuclei able to diffusion growth. So far, we use the model which assumes that critical nuclei of all phases, allowed by the phase diagram, appear at once (the unlimited nucleation model). It is known that the growth of a new phase from the nucleus is energetically favorable only in case of nucleus size exceeding some critical value l_{cr}, determined from extremal condition of Gibbs thermodynamic potential. In a one-component substance the extremality is expressed simply by the derivative of G with respect to the nucleus size being equal to zero: $\dfrac{\partial G}{\partial R}\bigg|_{l_{cr}} = 0$. At nucleation in the binary system there are some problems concerning the difference between the composition of a nucleus and that of initial "parent" phases, occurring in general case [12]. Thus, the notions of the smallest (equilibrium), most probable and critical nuclei do not coincide. This matter is treated in more details below. For the present, the actual existence of the critical nucleus size is important for us, this critical size becoming unstable against decomposition at $1 < l_{cr}$.

We assume that at the initial period, successive layers of critical nuclei of all phases, allowed by phase diagram, appear as a result of heterophase fluctuations. It is significant that the nuclei arise in the chemical potential gradient field, so that finite differences $\Delta\mu$ over the thickness of each layer exist from the very beginning. Chemical potential gradients inside the nuclei cause diffusion fluxes through them. Owing to the difference in diffusivities, flux densities vary for different phases. The jumps of diffusion fluxes at interfaces make the boundaries move: if phase 1 provides more A atoms to the interface 1-2 than phase 2 takes, the interface will shift – phase 1 will grow at the expense of phase 2. At that nuclei layers come into diffusion interaction. The result of the interaction varies for different phases and depends on diffusion characteristics of all phases in phase diagram. Those phases, for which $\dfrac{-D\Delta c}{\Delta x}$, start growing and reach the observed phase layers. The nuclei of those phases, for which $\left.\dfrac{d\Delta x}{dt}\right|_{I_{cr}}$, reduce, become subcritical and decay. The new ones arise at their place, and they suffer the same fate: they become exhausted and consumed by fast-growing neighbouring phases (“vampires”).

The growth of such phases is suppressed, they exist in the contact zone only “virtually”, in the form of nuclei that appear and decay straight away. This explains the disagreement between the phase composition of the zone and phase diagram. Criteria of suppression and growth for the simplest cases will be obtained in the next section.

Yet, the phase suppression, as it will be shown in 1.3, lasts for the finite period of time (though it may be quite a long one). When growing phases amount to a certain thickness and the fluxes through them $\dfrac{-D\Delta c}{\Delta x}$ are reduced sufficiently, the value $\left.\dfrac{d\Delta x}{dt}\right|_{I_{cr}}$ for the previously suppressed phase gets positive, so that it starts growing as well. It is confirmed by the experiment [2]. The time of nuclei suppression actually presents the incubation time of a phase (if not taking into account the time of nuclei formation). Examples of calculations are given in 1.3.

Thus, our model shows that, at external influences being absent in non-limited diffusion couple, all phases allowed by phase diagram must eventually grow (this doesn't concern thin films). In [5, 6] it is stated that every time quite a small fraction of all phases, allowed by phase diagram, grows. This conclusion in incorrect. In fact, during traditional investigation periods, involved in experiments, not all phases arise. And our model provides explanation for this. But if the periods are very long other phases must also appear. As mentioned, it was experimentally proved [2], for the phase that had been absent, arose in the zone only after annealing for hundreds of hours.

When the previously suppressed phase starts growing, its own “building process” requires some material that in other case would be used for the extension of other layers. This means that in the moment the suppressed phases start their growing, the growth kinetics of other phases acquires some peculiarities. The latter are briefly analyzed in [3].

The above-described situation seems to be logically clear. However, nature is not obliged to keep to our logic. It may be quite a real case, at which for some

reasons the nuclei formation in some phases rather than phase growth from the nuclei is opposed; while the emergence of nuclei in metastable phases may appear to be easy, and these nuclei may start growing and suppressing the nuclei of "legal" stable phases, which had appeared subsequently. The conditions for formation of these stable phases' nuclei depend on the type of neighbouring phases and therefore are considered the "parent" ones. Eventually, the solid phase chemical interaction becomes highly complicated and turns to be strongly dependent on random factors arising at the initial stage of the contact.

2. Criteria of phase growth/suppression (approximation of unlimited nucleation). Let's treat the initial stage of phase formation at annealing of the diffusion couple A-B, regarding the phase diagram to include two intermediate phases 1 (c_1, $c_1+\Delta c_1$) and 2 (c_2, $c_2+\Delta c_2$), and neglecting the solubilities of A in B and B in A. The concentration profile can be depicted from Fig. 1.2 (see previous).

Then the equations of diffusion interaction between phases are of the following form:

$$(c_1 - 0)\frac{dx_{A1}}{dt} = -\frac{D_1\Delta c_1}{\Delta x_1}$$

$$(c_2 - c_1)\frac{dx_{12}}{dt} = \frac{D_1\Delta c_1}{\Delta x_1} - \frac{D_2\Delta c_2}{\Delta x_2} \qquad (2.1)$$

$$(1 - c_2)\frac{dx_{2B}}{dt} = \frac{D_2\Delta c_2}{\Delta x_2} .$$

According to the accepted model, the layers of critical nuclei of both phases appear in the contact zone at the very initial stage. From Eq. (2.1), the expressions for phase thicknesses $\Delta x_1 = \Delta x_{12} - \Delta x_1$, $\Delta x_2 = \Delta x_{2B} - \Delta x_{12}$ follow:

$$\frac{d\Delta x_1}{dt} = \frac{1}{c_2 - c_1}\left(\frac{c_2}{c_1}\frac{D_1\Delta c_1}{\Delta x_1} - \frac{D_2\Delta c_2}{\Delta x_2}\right)$$

$$\frac{d\Delta x_2}{dt} = \frac{1}{c_2 - c_1}\left(-\frac{D_1\Delta c_1}{\Delta x_1} + \frac{1-c_1}{1-c_2}\frac{D_2\Delta c_2}{\Delta x_2}\right). \qquad (2.2)$$

Simple analysis of equalities (2.2) shows that the phase behaviour is determined by the value of dimensionless parameter

$$r = \frac{D_1\Delta c_1 l_{cr}^{(2)}}{D_2\Delta c_2 l_{cr}^{(1)}} .$$

1. At $r < \dfrac{c_1}{c_2}$ we get: $\left.\dfrac{d\Delta x_1}{dt}\right|_{l_{cr}} < 0, \left.\dfrac{d\Delta x_2}{dt}\right|_{l_{cr}} > 0$, that is phase layer 2 grows

from the very beginning, suppressing the growth of phase 1 nuclei (phase 2 is a "vampire")

2. At $\dfrac{c_1}{c_2} < r < \dfrac{1-c_1}{1-c_2}$ we get: $\left.\dfrac{d\Delta x_1}{dt}\right|_{l_{cr}} > 0, \left.\dfrac{d\Delta x_2}{dt}\right|_{l_{cr}} > 0$, i.e. both phase layers

grow from the beginning.

3. At $r > \dfrac{1-c_1}{1-c_2}$ we obtain: $\left.\dfrac{d\Delta x_1}{dt}\right|_{l_{cr}} > 0, \left.\dfrac{d\Delta x_2}{dt}\right|_{l_{cr}} < 0$, that is phase layer 1

grows from the beginning, suppressing the growth of phase 2 nuclei (phase 1 is a "vampire")

Thus, the criterion for the suppression and growth of phases at the initial stage for the system A-1-2-B is obtained; it is convenient to represent it on the diagram (see Fig. 2.1).

The numbers denote those phases that grow from the very beginning. Similarly, we can find the criteria for the suppression and growth in case of three intermediate phases between mutually insoluble A and B.
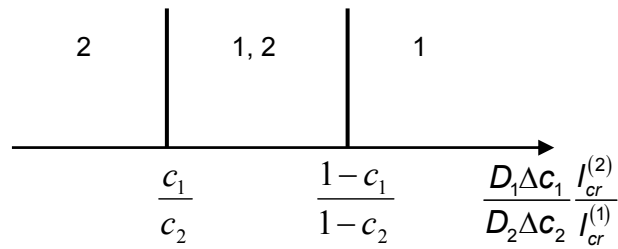

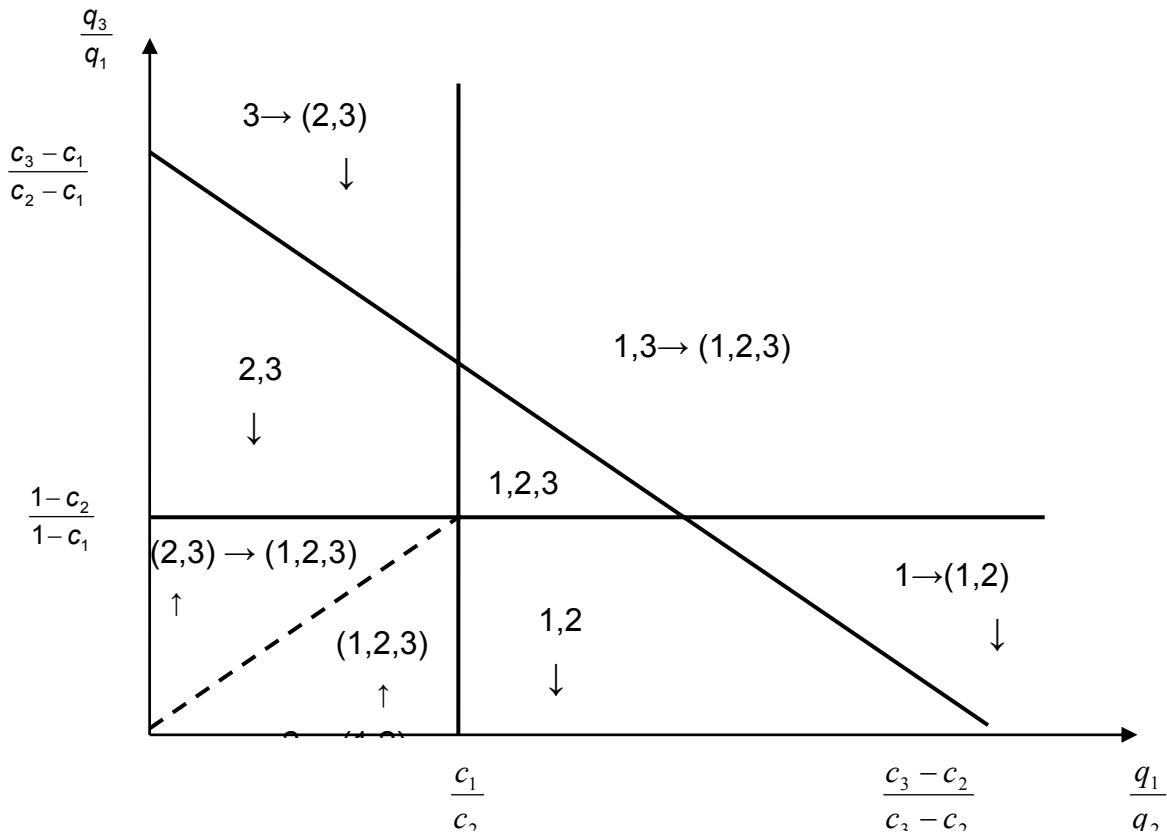Fig. 2.1. Suppression and growth criteria for two intermediate phases.

Fig. 2.2. Suppression and growth criteria: case of three intermediate phases.

The corresponding graphical representation of the criterion is given on Fig. 2.2. The arrows indicate the sequence of phase composition change in the diffusion zone.

3. Incubation time

As it was told in the first paragraph, phase suppression cannot be everlasting. Let's again view system B for the case of $r > (1-c_1)/(1-c_2)$, when at the initial point of time the nuclei of phase 2 are "exhausted" by the growing phase 1. One can easily check that the growth of the single phase 1 between insoluble A and B takes place according to the following law:

$$\Delta x_1 = \left(\frac{2D_1 \Delta c_1}{c_1(1-c_1)} \right)^{1/2} t^{1/2} \tag{3.1}$$

At that critical nuclei of the phase 2 are constantly arising at the boundary of the growing phase 1 and B. Taking (2.2) into account the rate $d\Delta x_2 / dt$ for these nuclei is determined by the equality:

$$\left. \frac{d\Delta x_2}{dt} \right|_{l_{cr}} = \frac{1}{c_2 - c_1} \left(-\frac{D_1 \Delta c_1}{\Delta x_1} + \frac{1-c_1}{1-c_2} \frac{D_2 \Delta c_2}{l_{cr}^{(2)}} \right). \tag{3.2}$$

As the thickness Δx_1 increases, such a moment comes when the value $\left. \frac{d\Delta x_2}{dt} \right|_{l_{cr}}$ passes through zero and becomes positive, i.e. phase 2 will no longer be suppressed. This will occur at:

$$\Delta x_1 = \frac{1-c_2}{1-c_1} \frac{D_1 \Delta c_1}{D_2 \Delta c_3} l_{cr}^{(2)}, \tag{3.3}$$

that is, according to (3.1), the time point for this is:

$$\tau_2 = \frac{c_1(1-c_2)^2}{2(1-c_1)} \frac{D_1 \Delta c_1}{(D_2 \Delta c_2)^2} \left(l_{cr}^{(2)} \right)^2 \tag{3.4}$$

It is quite natural for the time τ_2 of phase 2 suppression to be referred to as incubation time, if disregard the time of first critical nuclei formation.

If $D_i \Delta C_i$ at least approximately fit the Arrhenius dependence ($(\exp(-Q/kT)$, for more details see [1]), then:

$$\exp \frac{2Q_2 - Q_1}{kT} \tag{3.5}$$

one may expect $Q_2 > Q_1/2$, so that incubation time must reduce with temperature growth. If, by chance, $Q_2 < Q_1/2$, it should mean that the barriers for atom jumps in phase 2 are much lower than those in phase1, so at commensurate pre-exponential factors one may expect the diffusivity of phase 2 to be much higher than that of phase1, $D_2 \Delta C_2 \gg D_1 \Delta C_1$, and phase 2 will appear to be not the suppressed phase but the suppressive one (a "vampire"), the growth of phase 1 will be opposed and its incubation time will reduce with the growth of *T*. Let's specify the calculation of the critical nucleus value. Consider the formation of phase1 nucleus at the plane interface *α* and *β*. The formation involves Gibbs bulk energy gain:

$$n(g_\alpha - g_1)V_\alpha + n(g_\beta - g_1)V_\beta$$

and surface energy loss $\sigma_{\alpha 1} S_{\alpha 1} + \sigma_{1\beta} S_{1\beta} - \sigma_{\alpha\beta} S_{\alpha\beta}$ connected with the change of α-β contact to two contacts α-1 and 1-β ($\sigma_{\alpha 1}$, $\sigma_{1\beta}$, $\sigma_{\alpha\beta}$ – interface tension coefficients). From considerations of symmetry (disregarding anisotropy of phase lattices) the basis of the nucleus can be treated as a circle of a certain radius R ($S_{\alpha\beta} = \pi R^2$). Similarly to the nucleus at the boundary of two identical grains (see [13]) it's quite easy to find boundary angles and dependences of ΔG on R:

$$\cos \vartheta_\alpha = \frac{(\sigma_{\alpha\beta}^2 + \sigma_{\alpha 1}^2 - \sigma_{1\beta}^2)}{2\sigma_{\alpha\beta}\sigma_{\alpha 1}}, \tag{3.6}$$

$$\cos \vartheta_\alpha = \frac{(\sigma_{\alpha\beta}^2 + \sigma_{1\beta}^2 - \sigma_{\alpha 1}^2)}{2\sigma_{\alpha\beta}\sigma_{\beta 1}}, \tag{3.7}$$

$$\Delta G = -\frac{\pi R^3}{3}\left\{ \frac{n(g_\alpha - g_1)}{\sin \vartheta_\alpha}\left(\frac{2}{1+\cos \vartheta_\alpha} - \cos \vartheta_\alpha \right) + \right.$$

$$\left. + \frac{n(g_\beta - g_1)}{\sin \vartheta_\beta}\left(\frac{2}{1+\cos \vartheta_\beta} - \cos \vartheta_\beta \right) \right\} +$$

$$+ \pi R^3\left(\frac{2\sigma_{\alpha 1}}{1+\cos \vartheta_\alpha} + \frac{2\sigma_{1\beta}}{1+\cos \vartheta_\chi} - \sigma_{\alpha\beta} \right) \tag{3.8}$$

The composition and components' chemical potentials of the appeared nucleus vary over X, which has radical influence on its fate. Thus, in the strict sense, while calculating ΔG one should take integrals of $\int n(g_\alpha - g_1)dV$ type instead of n(g$_\alpha$-g$_1$)V$_\alpha$. This was realized in [7, 33-40]. Now we consider C gradient to be small and function g(C) to vary insignificantly inside the nucleus, such that g$_1$ implies minimum of Gibbs potential (per one atom) for phase 1 (and g$_\alpha$, g$_\beta$ – Gibbs potentials of pure A and B).

From thermodynamic viewpoint, the nucleus is able to growth at R>R$_{cr}$, G(R) monotone decreasing with R increase. Though, it doesn't mean that neighbouring phases, also able to growth, will give it such an opportunity. Investigating extremal properties of the function (3.8), one can achieve:

$$R_{cr} = 2\cdot\frac{\dfrac{2\sigma_{\alpha 1}}{1+\cos \vartheta_\alpha} + \dfrac{2\sigma_{1\beta}}{1+\cos \vartheta_\beta} - \sigma_{\alpha\beta}}{\left\{ \dfrac{n(g_\alpha - g_1)}{\sin \vartheta_\alpha}\left(\dfrac{2}{1+\cos \vartheta_\alpha} - \cos \vartheta_\alpha \right) + \dfrac{n(g_\beta - g_1)}{\sin \vartheta_\beta}\left(\dfrac{2}{1+\cos \vartheta_\beta} - \cos \vartheta_\phi \right) \right\}} \tag{3.9}$$

Transversal size of the critical nucleus:

$$l_{cr} = R_{cr}\left(\frac{1-\cos \vartheta_\alpha}{\sin \vartheta_\alpha} - \frac{1-\cos \vartheta_\alpha}{\sin \vartheta_\beta} \right) \tag{3.10}$$

4. Should we rely upon the ingenuity of nature? Nucleation problems. Metaquasi-equilibrium conception. Until now we've been considering nature to be resourceful enough to always find the way (besides, a rather quick one) to fulfill heterogeneous fluctuations at intermediate phase nucleation. However, further we're going to consider such cases at which the time of intermediate phase nucleus formation may appear to be quite large. For the sake of simplicity we'll limit ourselves to the case of one intermediate phase. Note, that two fundamentally different situations are possible here. They are illustrated on Fig. 4.1a and Fig. 4.1b.
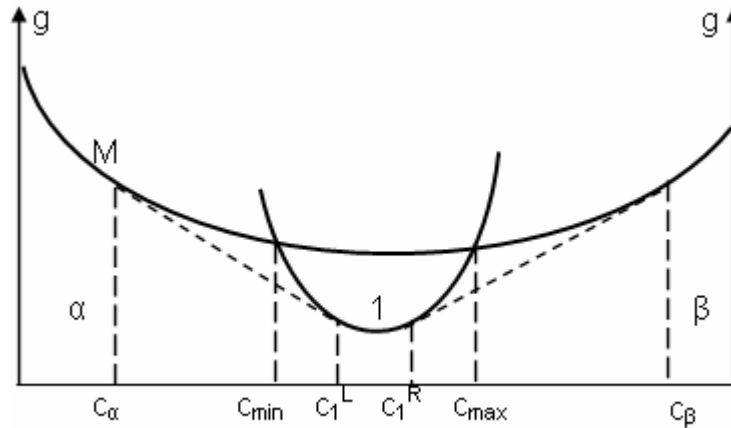
Fig. 4.1a. Dependence of Gibbs potential on the composition,
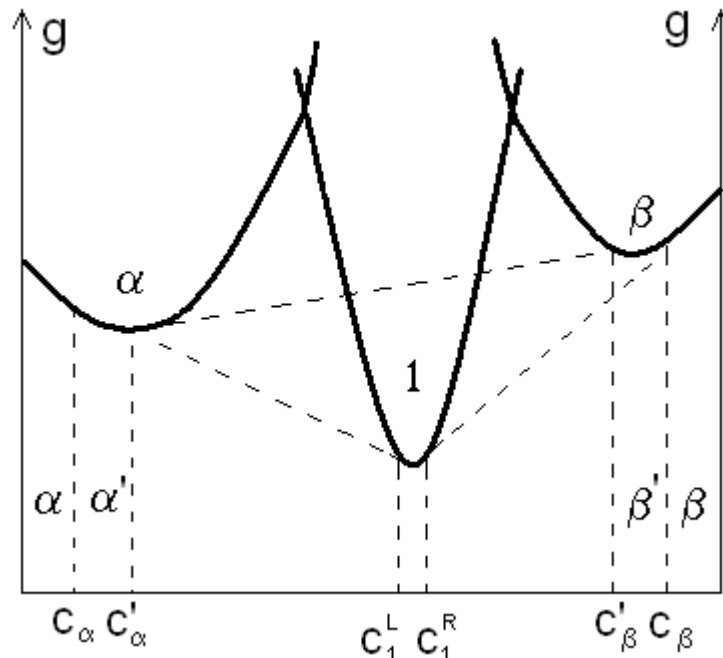case of total mutual solubility.

Fig. 4.1b. Dependence of Gibbs potential on the composition,
case of limited mutual solubility.

In case (a) there is a metastable solid solution M over the whole concentration interval, and an intermediate phase 1 (for instance, an ordered solution) is possible to appear which is thermodynamically more favorable in a certain concentration interval. It is significant that at annealing of A-B couple the M phase lattice exists from the very beginning while phase 1 is absent. The system isn't "aware" of a more favorable phase 1 up to fluctuation nucleation of a new lattice, so interdiffusion takes place within the single metastable phase M like any other quasi-equilibrium process (each physically small volume has enough time to relax to "equilibrium" state before its composition changes considerably). Since local relaxation reaches not truly equilibrium phases α, 1, β, but a metastable phase M, this process will be referred to as a metaquasi-equilibrium. As it is shown in the next section, even if neglect the time required for the lattice building, successful nucleation needs time for concentration preparation $\tau_1 \sim R^2 / D_M \Delta c_m$, R standing for the size of a new phase

viable nucleus, D_M being the interdiffusion coefficient in the "parent" phase M, Δc_m is a concentration interval inside which phase 1 is more favourable than phase M. At small D_M or Δc_m the time τ_1 may appear to be larger. Typical values are: $R \sim 10^{-7}$cm, $\Delta c_m \sim 10^{-2}$. If $D_M \sim 10^{-15}$cm^2/s, $\tau_1 \sim 10^3$s $\sim$ 15 minutes.

Nucleation in case (b) appears to be even more complicated. Here the lattices of α and β phases do not continuously change one into another and "concentration preparation", i.e. formation of the interval Δx with concentrations (c_c^L, c_1^R) by way of interdiffusion, in which only lattice transformation remains to be done, is impossible at all.
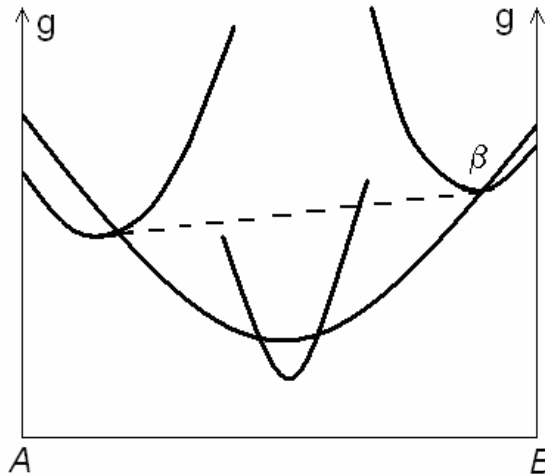

Fig. 4.2. Illustration of possibility for intermediate phase1 formation from limited solid solutions via intermediate stage of amorphous phase with total solubility.

Indeed, until the nuclei of phase 1 appear the system isn't "aware" of its profit and is supposed to establish quasi-equilibrium between initially existing α and β phases. This means that quasi-equilibrium boundary concentrations c'_α and c'_β will set in locally at the moving interface after initial kinetic period. These concentrations are determined by general tangent to the curves $g_\alpha(c)$ and $g_\beta(c)$. This quasi-equilibrium is not real (for it doesn't regard phase 1 which hasn't appeared yet), still it is not less steady. We'll again call it metaquasi-equilibrium. It is important that here the interdiffusion process will never make up the concentration intervals from c'_α to c'_β including ($c_1, c_1+\Delta c_1$), corresponding to intermediate phase. Thus, it turns out that we obtain, at first sight, a paradoxical case – the legal phase 1 cannot arise despite its total thermodynamic favorability.

In the context of the "refined", free-of-drawbacks approach, only one way can be proposed: concentration zones from c_α to c'_α (α') and from c'_β to c_β (β'), formed in the process of metaquasi-equilibrium diffusion, are relatively unstable and must eventually decay: α' into α+1, β' into β+1. At that, the problem of intermediate phases rise at interdiffusion is reduced to the problem of supersaturated solid solutions decomposition. . Thermodynamic analysis of this situation was made in [39]. The kinetic difficulties here are presented by concentration supersaturations c'_α-c_α and c_β-c'_β which may turn out to be quite small if compared to the difference required for new phase formation.

The probability of concentration fluctuation in a binary system is

$$W(\delta c) \sim \exp\left(-\frac{Ng''(\delta c)^2}{2kT}\right),$$

where g'' is the second derivative of Gibbs potential with respect to atomic concentration C for the phase in which the fluctuation occurs, N – number of atoms involved in concentration fluctuation.

For the systems with very low solubility $g_\alpha'' \sim kT/c_\alpha$. At $\delta c \sim 1/2$, $N \sim 100$, $c_\alpha \sim 10^{-2}$ we get: $W \sim \exp(-1250)$.

One may expect such fluctuation for $\tau \sim \dfrac{l^2}{D_\alpha W}$. At $l \sim 10^{-7}$cm, $D_\alpha \sim 10^{-12}$cm^2/s one gets $\tau_1 \sim 10^{400}$ s which is absolutely unbelievable.

Hence, concentration preparation by way of fluctuation in case (b) at low solubility of A and B is of very low probability. But the phases still appear in the diffusion zone, so the concentration preparation is realized, though, not for all but for many phases.

We can presuppose the following possibilities:

1. At the intermediate stage there occurs the rise of metastable phase (amorphous, for instance), concentration range, where concentration preparation takes place, being rather wide,. For this the curves of Gibbs phase potentials must be arranged as indicated by Fig. 4.2.

The formation of the metastable phase itself is facilitated by, first, its greater "overlapping" with α, β- phases, and by the possibility of its nucleation as a result of segregation at grain boundaries or interfaces.

2. Formation of a zone with concentrations required for the intermediate phase resulting from the processes of such a type as "cold homogenization" or diffusion-induced grain boundary migration (DIGM).

3. Formation of concentration-prepared zones proceeding from segregation at grain boundaries or other defects.

4. High interface tension of α and β phases leads to the following: the size of the intermediate phase critical nucleus doesn't exceed the interatomic distance. This is correct anyway when

$$\sigma_{\alpha\beta} > \sigma_{\alpha 1} + \sigma_{1\beta}$$

(see, for example, F.d'Heurle's review [14]).

In this case Gibbs potential starts decreasing as the nucleus size grows from zero thickness. Here the following situation seems to be quite appropriate: first, the 2-dimensional nucleus of the surface intermediate phase appears at the interface, to which the atoms from the phase bulks attach, so that 2-dimensional nucleus continuously acquires a form of a 3-dimensional phase layer.

The authors realize that the proposed alternatives lack reasonable numerical estimations to obtain a firm basis, thus, don't pretend to any final explanations but simply to formulation of the problem and some stimulating speculations.

5. Suppression of intermediate phase by solid solutions. Incubation time for intermediate phases at interdiffusion can be stipulated not only by diffusion suppression of their nuclei by neighbouring phases. The necessity of "concentration preparation" for transformation of metastable formations can also influence this time. At solid phase reactions when intermediate layers form and grow in the contact zone of two metals, the phase composition of the diffusion zone in many cases appears to be incomplete if compared to phase diagram (see, for example, [15, 1]). As shown above (see [3]), this disagreement is temporary for massive samples, and it is connected with diffusion suppressions of critical nuclei of some intermediate phases, realized by neighbouring fast-growing phases. For the case of competition between

two or three intermetallics, the suppression and growth criteria are already obtained above. The suppression time for the nuclei of the phases being suppressed, was also found. It is the time that was considered the phase's incubation time. It was assumed that the nuclei themselves appear in the contact zone almost immediately (as a result of heterophase fluctuations). This assumption doesn't always prove to be correct. Let's analyze the problem of incubation time taking into account the finite rate of nuclei formation by the example of a single intermediate phase 1 ($c_1 < c < c_1 + \Delta c_1$) between solid solutions α ($0 < c < \Delta c_\alpha$) and β ($1 - \Delta c_\beta < c < 1$).

Unlimited nucleation. So, due to heterophase fluctuations, the nuclei of intermediate phase 1 between α and β must appear. The appearance of intermediate phase nucleus is thermodynamically favorable only if its size exceeds the critical value l_{cr}. Our case is complicated by the fact that the nucleus appears in the system which hasn't been homogeneous from the very beginning. So, the nucleus appears in the conditions of chemical potential and concentration gradients. And the driving force of the process is connected with concentration supersaturation rather than with overcooling (though, there is a certain interrelation between them). This makes the composition of nuclei non-homogeneous from the very beginning. Thus, when calculating points of extremum for Gibbs potential, one must use integrals of this $\int_{x_L}^{x_R} g(c(x))S(x)dx$ type with varying limits (S(x)x – variable cross-section area of a nucleus).

Besides, it should also be borne in mind that at essential overcooling (supersaturation) there is a higher possibility of polymorphic transformation without any composition change, diffusion of atoms being slow. Apparently, in general case the problem presents difficulties which was considered in much more details in [7, 33-40]. Here we'll limit ourselves to a case of narrow intermediate phases where Gibbs potential g(c) almost doesn't change within a narrow homogeneity range Δc (though, derivatives $\partial g / \partial c$ may change significantly, (see, for example, [16]). In this case all three kinds of nuclei reduce to a single notion of a critical nucleus, defined from the extremal principle of Gibbs thermodynamic potential for a system with a nucleus.

For a phase to grow a critical nucleus must appear. As stated above, unlike phase transformations in a homogeneous system, we deal with the nuclei arising in chemical potential gradient field. "On the left" we have a nucleus approaching equilibrium with phase α, "on the right" – with phase β. Therefore, diffusion fluxes pass through it. Jumps of diffusion fluxes, occurring at the boundaries α–1 and 1–β, cause boundary motion, i.e. change of the nucleus' size. If critical nucleus becomes smaller (($d\Delta x/dt)l_{cr} > 0$), then the phase starts growing. Suppose D_α, D_l, D_β are effective diffusion coefficients in phases α, l, β. Let nuclei of phase 1 form a layer of $\Delta x_1 = l_{cr}$ thickness between α and β. Considering Δc_α, Δc_1, $\Delta c_\beta << 1$, put down the equation of flux balance at moving phase boundaries:

$$(c_1 - \Delta c_\alpha)\frac{dx_{\alpha 1}}{dt} = \frac{D_\alpha \Delta c_\alpha}{\sqrt{\pi D_\alpha t}} - \frac{D_1 \Delta c_1}{l_{cr}}$$

$$(1 - \Delta c_\beta - c_1 - \Delta c_1)\frac{dx_{1\beta}}{dt} = \frac{D_1 \Delta c_1}{l_{cr}} - \frac{D_\beta \Delta c_\beta}{\sqrt{\pi D_\beta t}} \quad . \tag{5.1}$$

(When the smallness conditions of Δc_α, Δc_β are violated, the Eqs. (5.1) become roughly correct). For $\Delta x_1 = x_{\beta 1} - x_{\alpha 1}$ from (5.1) we get:

$$\frac{d\Delta x_1}{dt}\bigg|_{l_{cr}} \cong \frac{1}{c_1(1-c_1)} \frac{D_1\Delta c_1}{l_{cr}} - \frac{\left(\dfrac{\Delta c_\alpha}{c_1}\sqrt{D_\alpha} + \dfrac{\Delta c_\beta}{1-c_1}\sqrt{D_\beta}\right)}{\sqrt{\pi t}} \qquad (5.2)$$

As it follows from (5.2), the value $(d\Delta x / dt)_{l_{cr}}$ becomes positive, and growth of phase 1 is allowed at

$$t > \tau_1 = \left[\frac{\Delta c_\alpha(1-c_1)\sqrt{D_\alpha} + \Delta c_\beta c_1\sqrt{D_\beta}}{D_1\Delta c_1} \frac{l_{cr}}{\sqrt{\pi}}\right]^2 . \qquad (5.3)$$

The suppression time τ_1 of phase 1 growth from the nuclei can be called incubation time, if neglect time required for nuclei formation.

Finite rate of nuclei formation. Two fundamentally different cases, shown in Fig. 4.1, are possible. Here we'll examine the case α in greater detail. Phases α and β have identical lattice and belong to a one metastable formation of solid solution. In this case before a nucleus of phase 1 appears interdiffusion proceeds as a usual quasi-equilibrium process in a one-phase system. We've agreed to term the processes of this kind taking place in metastable system as metaquasi-equilibrium ones.

While analyzing the diagram in the figure, one can hypothesize that concentration range of metastable formation between the points M and N (that is c_1' and $c_1' + \Delta c_1'$) serves as "initial material" for phase 1 formation by way of polymorphic transformation. However, after the nucleus of phase 1 has appeared, concentration ranges $\Delta c_\alpha - c_1$ and $c_1 + \Delta c_1 - 1 - \Delta c_\beta$ turn out to be unstable and correspond to two-phase regions on phase diagram. But according to Gibbs phase rule these regions don't appear in the diffusion zone as they are used in formation of the initial layer of phase 1. If the conditions of non-suppression of phase growth are fulfilled for this initial layer, an ordinary quasi-equilibrium process of phase layer growth proceeds due to diffusion interaction with solid solutions at its boundaries.

Thus, we presuppose that there are three stages of the process:

1)   appearance of metastable compound, call this stage "concentration" preparation;

2)   appearance of new phase nuclei, disappearance of unstable formations and creation (at their expense) of a new stable phase layer (under certain conditions);

3)   diffusion phase growth due to interaction with solid solutions.

Let's estimate the duration of the first stage. Concentration profile $c(x)$ in metastable formation must become so flat that the length exceeding l_{cr}: $x(c_1+\Delta c_1)-x(c_1)>l_{cr}$, i.e. $\Delta c_1/(\partial c/\nabla x\ )>l_{cr}$, will be found within the interval of thermodynamically favorable (for phase 1) concentrations $(c_1, c_1+\Delta c_1$. Here l_{cr} indicates the thickness of the initial layer. Suppose, D^M is interdiffusion coefficient in metastable solution. Let $c_1,\sim1/2$. In the approximation $D^M=const$ $\partial c^M/\partial x \cong \exp(- x^2/4D^M t)/\sqrt{\pi D^M t}$, $c\sim1/2$ corresponds to $x\sim0$, so that $(\partial c/\partial x)_{c\sim1}\sim(\pi\ D^M t)^{1/2}$. So, the condition of concentration readiness for phase 1 growth becomes $\Delta c_1(\pi D^M t)^{1/2}\geq l_{cr}$, so that

$$\tau_{prep} \approx l_{cr}^2/\pi D^M (\Delta c_1)^2 . \qquad (5.4)$$

The value of D^M for metastable phase can be estimated by the method, proposed in [17].

Here we shall not regard the time of lattice reconstruction. Then the time of diffusion suppression of phase 1 nuclei can be considered as incubation time (5.3), provided it is larger than the time of concentration preparation for critical nucleus appearance τ_{prep}:

$$\left[\frac{\Delta c_\alpha (1 - c_1)\sqrt{D_\alpha} + \Delta c_\beta c_1 \sqrt{D_\beta}}{D_1 \Delta c_1} \right]^2 \frac{I_{cr}^2}{\pi} > \frac{I_{cr}^2}{\pi D^M (\Delta c_1)^2} . \tag{5.5}$$

If the condition (5.5) fails, i.e. diffusion permeability of phase 1 is high enough and its nuclei are competitive, concentration preparation time becomes equal to incubation time (5.4).

Rigorous theory of nucleation in the concentration gradient and its influence on the incubation period and phase competition was built by Gusak, Desre and Hodaj in the series of papers [7, 33-40].

6. Phase competition in a model of divided couple. The problem of obtaining and suppression of intermediate phases presents special interest when realized at solid-phase reactions in powder mixtures. Consider the initial stage of sintering of the simplest binary mixture when the particles of initial components still preserve independence and one can speak of two connected surfaces with different total squares S_A, S_B, brought into contact via fast surface diffusion and diffusion through the gas phase. For simplicity, let's take a system of two almost mutually insoluble components, giving two intermediate phases with concentrations c_1, c_2 and narrow homogeneity ranges Δc_1, $\Delta c_2 \ll 1$ on the phase diagram. We'll consider surface diffusion of both components to be fast enough to have equal chemical potentials at each point of both surfaces at each time point. When both phases grow simultaneously we may have the situations illustrated by schemes *b,c,d* on Fig. 6.1. If one of two phase is suppressed, cases *a, e* are implemented.

Obviously, at the initial stage the nuclei of phase 1 must appear on the surface of A and nuclei of phase 2 – on the surface of B. Their further destiny is stipulated by diffusion phase competition, the theory of the latter being set out above. Main principles of the theory will be employed in the present section.

We'll limit ourselves to small times of annealing, when the thickness of growing phases is much less than the size of particles R, so that we could use planar geometry. As is it known [9], in general case the rate of phase layer growth is determined both by diffusion transfer and the rate of reaction at interfaces (flux through the interface between *i-th* and (*i*+1)-*th* phases is $j = k_{i,i+1}\delta c$, where δc - boundary concentration deviation from the equilibrium value, $k_{i,i+1}$ - reaction rate constant). Flux through the *i-th* phase may be expressed as

$$j = \frac{D_i \Delta c_i}{\Delta x_i + D_i / k_i},$$

where D_i is the effective interdiffusion coefficient, k_i is a so called effective constant of reaction rate: $1/k_i = l/k_{i,i+1} + l/k_{i-1,i}$. So far, we take a case of diffusion kinetics, when phase thicknesses D_i/k_i typical for boundary kinetics don't exceed the sizes of critical nuclei. Thus, the effect of final reaction rate at interfaces can be neglected from the very beginning.
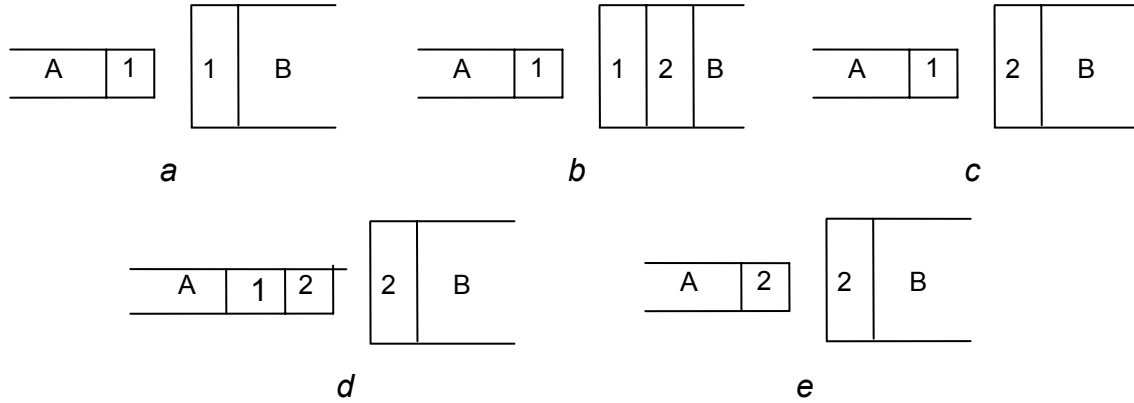
Fig. 6.1. Possible variants of growth and suppression of intermediate phases 1, 2 on free surfaces A and B being in ideal diffusion contact.

One can easily put down the system of balance equations for interface movement in case *c*. In the approximation of the flux steadiness over the growing phase layer, balance equations at moving interfaces are

$$\frac{dx_{A1}}{dt} = \frac{1}{c_1}\frac{D_1\Delta c_1}{\Delta x_1}, \frac{1}{\Omega_1}\left(-\frac{D_1\Delta c_1}{\Delta x_1} - u_1 c_1\right)S_A = \frac{1}{\Omega_2}\left(-\frac{D_2\Delta c_2}{\Delta x_2} - u_2 c_2\right)S_B,$$

$$\frac{1}{\Omega_1}u_1 S_A = \frac{1}{\Omega_2}u_2 S_B, \frac{dx_{2B}}{dt} = \frac{1}{1-c_2}\frac{D_2\Delta c_2}{\Delta x_2}, \qquad (6.1)$$

where $\Omega_1, \Omega_2, \Omega_{B(A)}$ - atomic volumes of phases and material B(A). Here we regard interface mobility between phases 1, 2 and a gas phase (u_1, u_2 – boundary rates). Kirkendall effect is neglected. Eqs. (6.1) easily result in the simple phase interaction picture:

$$\frac{d\Delta x_1}{dt} = \frac{1}{c_2 - c_1}\left(\frac{c_2}{c_1}\frac{D_1\Delta c_1}{\Delta x_1} - \frac{\Omega_1}{\Omega_2}\frac{S_B}{S_A}\frac{D_2\Delta c_2}{\Delta x_2}\right),$$

$$\frac{d\Delta x_2}{dt} = \frac{1}{c_2 - c_1}\left(-\frac{\Omega_2}{\Omega_1}\frac{S_A}{S_B}\frac{D_1\Delta c_1}{\Delta x_1} + \frac{1-c_1}{1-c_2}\frac{D_2\Delta c_2}{\Delta x_2}\right). \qquad (6.2)$$

At the "initial point of time" we may assume $\Delta x_1 = l_{cr}^{(1)}, \Delta x_2 = l_{cr}^{(2)}$, l_{cr} standing for critical size of the nucleus. In many cases $l_{cr}^{(1)}$ and $l_{cr}^{(2)}$ can be considered equal by the order of magnitude. If the inequality

$$\frac{1-c_1}{1-c_2} > \frac{\Omega_2}{\Omega_1}\frac{S_A}{S_B}\frac{D_1\Delta c_1}{D_2\Delta c_2} > \frac{c_1}{c_2}, \qquad (6.3)$$

is fulfilled, both phases grow from the very beginning, obeying the parabolic law at $R \gg \Delta x \gg l_{cr}$. Having solved the system (6.2) for this case, we find out that the ratio of volumes for growing phases is time-constant and equals

$$\frac{V_2}{V_1} = \frac{S_B\Delta x_2}{S_A\Delta x_1} = \frac{r\varphi^2 - 1 + \sqrt{(r\varphi^2)^2 + 4r\varphi\frac{c_2}{c_1}\frac{1-c_1}{1-c_2}}}{2\frac{c_2}{c_1}}, \qquad (6.4)$$

where $r = (D_2\Delta c_2)/(D_1\Delta c_1), \varphi = \Omega_1/\Omega_2 \cdot S_B/S_A$.

Hence, the ratio of volumes is determined by $r\varphi^2$, i.e. not only by diffusion coefficients but by "relative dispersivity" S_B/S_A as well. At $r\varphi^2 \ll 1$ and $r\varphi^2 \gg 1$ the dependence of V_2/V_1 on $r\varphi^2$ asymptotically approaches the lines with slopes $(1-c_1)/(1-c_2) > 1$ and $c_1/c_2 < 1$, respectively. Of course, the dependence (6.4) was obtained within a quite rough model under the conditions S_B/S_A = const, $l_{cr} \ll \Delta x_i \ll R$, which are violated with time. Actually, we can hardly expect V_2/V_1 to be time-constant but the conclusion about the character of V_2/V_1 dependence on S_B/S_A and on $D_2\Delta c_2/D_1\Delta c_1$ must remain correct.

If inequality (6.3) fails, and, for example

$$\frac{\Omega_2}{\Omega_1} \frac{S_A}{S_B} \frac{D_1\Delta c_1}{D_2\Delta c_2} > \frac{1-c_1}{1-c_2},$$

then $\left.\dfrac{d\Delta x_2}{dt}\right|_{l_{cr}}$ in Eqs. (6.2) is negative. This means that critical nuclei of phase 2 on the surface B will decompose into phase 1 and pure B, so that phase 2 will be suppressed. This will inevitably lead to switching from case b to case a, i.e. to growth of phase 1 layer on surface B.

At that, it can be shown that at boundaries of phase 1 and at interfaces between surfaces A and B with gas phase we'll have the intermediate concentration from the interval

$$c_1 < c_1' = c_1 + \frac{\Delta c_1}{1 + \left(\dfrac{S_B}{S_A}\right)^2 \dfrac{D_B}{D_A} \cdot \dfrac{1-c_1}{c_1}} < c_1 + \Delta c_1..$$

With some (incubation) time the nuclei of phase 2 between 1 and B will stop being suppressed and the change to case b will take place. Using the above given approximations and writing balance equation for cases a and b, taking into account the difference between partial diffusion coefficients D_1^A, D_1^B in phase 1, one can show that τ_2, i.e. time point at which the value becomes positive and the possibility of diffusion growth of phase 2 layer appears, is defined by the formula

$$\tau_2 = \frac{c_1(1-c_1)/\left(l_{cr}^{(2)}\right)^2}{2\Delta c_1\left(c_1 D_1^A + \left(\dfrac{S_B}{S_A}\right)^2 (1-c_1)D_1^B\right)}\left(\frac{D_1\Delta c_1}{D_2\Delta c_2} \frac{1-c_2}{1-c_1}\right)^2, \qquad (6.5)$$

i.e. it strongly depends on S_B/S_A.

Detailed analysis of all possible variants is quite intricate, therefore, it is not given here (details can be found in [31,32]). Instead, we'd like to stress to following. Varying the ratio S_B/S_A ("relative dispersivity"), one may, first, transfer from suppression of one phase to growth of both phases or suppression of another phase; second, achieve the required relation of volumes of growing phases without changing the volumes of initial components, and finally, change the incubation time of suppressed phases. For instance, if phase 2 is more high-melting and $D_2\Delta c_2 \ll D_1\Delta c_1$, so that in a usual diffusion couple it is suppressed, then, enlarging the free surface of B particles by way of grinding, it's possible to make this phase appear and grow already at the initial stage of sintering (for this we must have $S_B/S_A = (D_1\Delta c_1)/(D_2\Delta c_2)$) or at least reduce the time of suppression.

If the growth of both phases is controlled by boundary kinetics at the initial stage, i.e. phase thicknesses typical for this regime ($x_i^* = D_i/k_i$) exceed $l_{cr}^{(i)}$ considerably, expression for fluxes through phases, $D_i \Delta c_i / \Delta x_i$, should be changed into $D_i \Delta c_i / (\Delta x_i + D_i/k_i)$. This will alter the explicit expressions for growth kinetics and cause deviation from parabolic law.

However, general conclusions will remain untouched. For example, condition of simultaneous growth of two phases from the very beginning (Eq. (6.3)) will acquire the following form (at $x_i^* >> l_{cr}^{(i)}$):

$$\frac{1-c_1}{1-c_2} > \frac{\Omega_2 S_A}{\Omega_1 S_B} \frac{k_1 \Delta c_1}{k_2 \Delta c_2} > \frac{c_1}{c_2}$$

i.e. it strongly depends on S_B/S_A again.

A divided diffusion couple (for example, coaxial cylinders) can represent a model system for investigation. In this system α- and ε-brass could stand for A and B elements, β-brass – for intermediate element, and zinc atoms could realize diffusion contact in both directions.

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